

GLASS MATRIX COMPOSITE FOAMS CONTAINING METALLIC FIBRES PRODUCED BY MICROWAVE HEATING

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ABSTRACT

The application of microwave radiation as the heating source for the fabrication of glass foams reinforced with metallic fibres has been investigated. A soda-borosilicate glass powder was chosen for the matrix. The metal fibres were Hastelloy X fibres in volume concentration of 0, 2 and 10%. The fibre diameter and length were 8 μm and 100 μm , respectively. The microwave heating process was carried out in two different self constructed microwave applicators operating at the 2.45 GHz ISM frequency. The glass foamed during processing leading to $> 50\%$ spherical porosity. Adding metallic fibres to the glass matrix prevented it from fracturing during processing and resulted in a more even distribution of finer pores. It is proposed that porosity formed during microwave heating as a consequence of localised glass matrix overheating in correspondence with the presence of metal fibres. This was caused by the preferential microwave absorption exhibited by the Hastelloy X fibres themselves and by the micro-regions of the matrix heated well above the glass softening temperature. The combination of high porosity and metal fibre toughening leads to composites of high thermal shock resistance and thermal stability suitable for thermal protection systems. This was demonstrated in the present study by the Hastelloy X fibres preventing cracking and disintegration of the composites during processing.

1. INTRODUCTION

Some of the main advantages achievable using microwave radiation include very short processing times, due to rapid, selective and volumetric heating [1]. As far as glass matrix composites are concerned, short processing times can help preventing any undesirable reactions between the glass matrix and the reinforcing particles. Moreover, selective microwave absorption by one of the two phases, depending on dielectric properties mismatch, can lead to the formation of peculiar, novel structures at glass/inclusion interfaces [2].

Glass foams are useful for their thermal and acoustic insulating properties and their low densities [3,4]. Moreover, by tailoring the dielectric properties of foamed composites, it might be possible to produce building materials able to attenuate electromagnetic (EM) fields in a wide range of frequencies and low-thermal capacity heating elements to be used as "grilling plates" in microwave ovens.

In the present work, microwaves at the ISM (Industrial, Scientific, Medical) frequency of 2.45 GHz are used as the heating source for the preparation of glass matrix composite foams reinforced by metallic (Hastelloy X) fibres. The addition of metallic fibres to a glass matrix should increase fracture toughness of the composite, exploiting several mechanisms such as ductile deformation and crack bridging [5,6]. The theoretical background for the use of microwaves in silicate glass/metal composite systems and main results of the experimental investigation are presented in the following sections.

2. THEORETICAL BACKGROUND

In the general case, the power density in a dielectric subjected to microwave heating can be expressed by Eq. 1 [7]:

$$P_d = \omega \varepsilon_0 \varepsilon''_{eff} E_{rms}^2 + \omega \mu_0 \mu''_{eff} H_{rms}^2 \quad (1)$$

where $\omega=2\pi f$ (f = frequency of the incident microwave radiation), ϵ_0 = permittivity of free space, ϵ''_{eff} = effective loss factor (imaginary part of the complex permittivity of the material), E_{rms} = root mean square value of the local electric field, μ_0 = permeability of free space, μ''_{eff} = effective imaginary part of the complex permeability of the material, H_{rms} = root mean square value of the local magnetic field.

Thus, the power density inside the material depends on the external electromagnetic field and on the material itself, which, in its turn, affects the local value of the electric and magnetic fields. Moreover, the dielectric properties of the materials are dependent on temperature and, in general, microwave absorption increases if the system is given a higher mobility [8]. This is the case of most polymeric and glass materials, which, at temperatures higher than the glass transition temperature, increasingly couple with microwaves, eventually leading to unwanted thermal runaway phenomena [9].

As far as metals are concerned, their interaction with microwaves can be described, in a simplified version, by Eq. 2 [10].

$$\delta_s = \sqrt{\frac{2}{\sigma\omega\mu_0\mu_r}} \quad (2)$$

where δ_s is the skin depth, i.e. a measure of the portion of the material directly involved with the interaction with the microwaves, and σ is the electric conductivity of the material. Thus, a dispersion of fine metal particles in a dielectric matrix, provided the percolation limit is not reached, can behave similarly to a distribution of micro-heating elements, whose power is dependent on the electromagnetic field and on the electric and magnetic properties of the metal itself.

This effect has been exploited in the present study, allowing to selectively heat the metal particles, which thus locally raise the surrounding glass matrix temperature up to a level at which it starts coupling with microwaves, leading to rapid processing time.

3. EXPERIMENTAL

Materials

The glass used for the matrix was a borosilicate glass named VG98, which has the following chemical composition (wt%) [11]: 56.7SiO₂ -12.4B₂O₃-2.6Al₂O₃-17.5Na₂O-4.1CaO-2.1MgO-4.6TiO₂. The Hastelloy X fibres (Bekaert, Belgium) were of composition (in wt%) Ni(51%), Cr(22%), Mo (9%) and Fe (18%), and were received chopped at 1 mm length in polyvinylalcohol binder. Table 1 gives a selection of the properties of the glass matrix and of the Hastelloy X fibres used. Fibres were washed with water to remove the binder.

Table 1. Properties of the VG98 borosilicate glass and Hastelloy X fibres

Material	Density (g cm ⁻³)	Mean Particle Size (µm)	CTE (10 ⁻⁶ °C ⁻¹)	E (GPa)
Glass, VG98	2.57	5.5	10.65	74.8
Hastelloy X fibre	8.22	8 (diam.) x 1000 (length)	15	221

Cylindrical samples (diameter: 10 mm, height: 2 mm) were obtained by uniaxial pressing mixtures of glass powder and chopped fibres at room temperature at a pressure of 36.9 MPa. Green densities of ~ 60 % of the theoretical density were achieved.

Microwave Processing

The microwave heating process was carried out in two different self constructed microwave applicators operating at the 2.45 GHz ISM frequency. The microwave apparatuses mainly consists of a remote controlled power supply (SM1150T, Alter, Italy), a generator (magnetron TM030, Alter, Italy), a transmission line (WR340 + impedance matching devices), a tunable applicator (variable height) and a dedicated control system, and they have been described in previous works [12, 13]. These two resonant cavities are an overmoded cylindrical applicator [12] which allows the heat treatment of large samples, under controlled atmosphere or vacuum, and a single mode applicator [13] which allows to selectively expose the samples to the maximum of the electric or of the magnetic field. The electromagnetic field distribution was simulated by the software CONCERTO 2.0 (Vector Fields, UK,) and hereafter reported as an example for the latter applicator (Fig. 1).

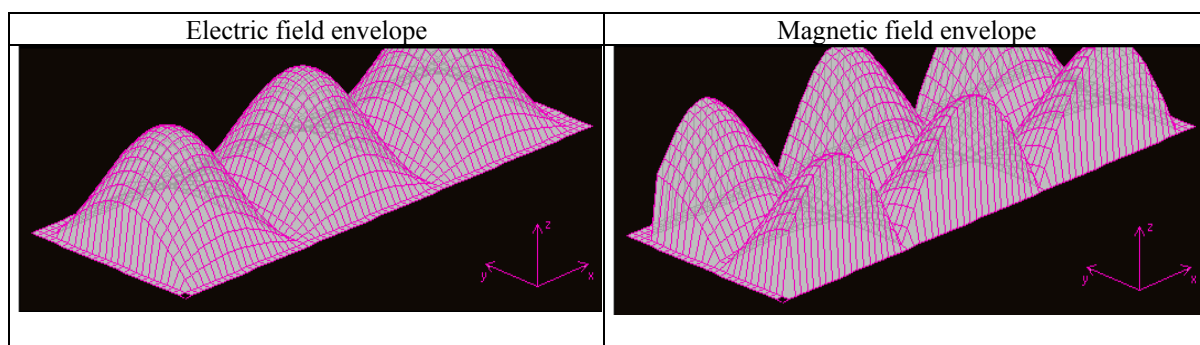


Fig.1. Electric and magnetic field envelope in the empty single-mode applicator - longitudinal median section

The magnetron output power can be continuously varied from 300 to 3000 W.

The glass/metal fibre composite samples were positioned, one per run, in a region of maximum electric or magnetic field, surrounded by aluminosilicate refractory lining belonging to the JM26 class, having an average thickness of 30 mm. Alumina powder was added to improve thermal insulation. The whole assemblage was axially inserted in the cylindrical applicator or perpendicularly in the single mode rectangular applicator. Heat-treatment was conducted according to the described setup, and also a complete series of samples was treated adding a SiC disc, as auxiliary absorber, in order to help raising the temperature of the samples presenting a low microwave coupling at room temperature.

Regarding the heating schedule, preliminary tests lead to the identification of 800 W as the maximum magnetron power output bearable by the samples without cracking during the microwave exposure. Under these conditions, a reflected power of 150-200 W was measured, leading to 600-650 W dissipated in the system. It is well-known that the samples integrity strictly depends on the temperature gradient, imposing an upper limit to how fast the load can be increased.

The final step of the heating treatment consisted of 5 minutes cooling by forced convection in the applicator. Heating and cooling were performed in Ar flux of 30 Nml/min. The complete densification process took 7 minutes for each sample. The procedure was repeated on three different sets of samples to verify the experimental reproducibility.

Temperature measurements were conducted in the single mode applicator by means of a MIKRON M680 optical pyrometer, connected to a sapphire fiber whose tip laid on (or was

inserted into) the sample. The applied and reflected microwave power was measured during the sintering process. Continuous tuning of the single mode applicator was required in order to compensate for the variation of the electric and dielectric properties of the load.

Characterisation

The density of samples after microwave processing was determined using the Archimedes' principle. The macrostructure and external appearance of the samples was characterised by low magnification optical microscopy and a digital camera. Selected samples were prepared for microscopic observation and quantitative microstructural analysis. These samples were cut, embedded in epoxy resin and polished using SiC paper and diamond paste (up to 1 μm). The microstructure of selected samples, both fracture surfaces and polished sections, was analysed by scanning electron microscopy (SEM) using a JEOL LV5160 instrument equipped with a backscattered detector.

4. RESULTS

Microwave heating with auxiliary absorber

Macroscopic visual examination revealed that during microwave processing using the SiC auxiliary absorber the samples without Hastelloy X fibres swelled and distorted. These samples also cracked into several pieces during cooling. Samples containing only 2vol% Hastelloy X fibres swelled and distorted but maintained their integrity, while samples containing 10vol% fibres underwent the least amount of swelling and distortion and also remained in one piece. All samples contained high levels of closed porosity. It was not possible to measure the density of the samples containing 0 vol% and 2vol% fibres using the Archimedes' principle as they had lower density than water. The relative density of the 2 vol% fibre containing samples was $< \sim 32\%$ (i.e. the sample contained $> 68\%$ porosity). For samples containing 10vol % Hastelloy X fibres, swelling was less severe and the density was measured to be 1.39 g/cm^3 , which corresponds to a relative density of 45% (55% porosity). Fig. 2. shows a macrograph of a sample containing 10vol% fibres which indicates low dimensional distortion.



Fig. 2. Macrograph showing final shape of the sample containing 10 vol% fibres after microwave processing

A visual examination of sectioned samples revealed a highly irregular distribution of large pores in samples containing 0 vol% and 2vol% Hastelloy X fibres, some pores were greater than 1mm in diameter. In contrast, the pore distribution in the composite containing 10vol% stainless steel fibres was more uniform, and the pores were much smaller, the largest pores having a diameter $< 0.2\text{mm}$.

SEM micrographs of the foam composites containing 10vol % and 2vol % Hastelloy fibres are shown in Fig. 3a. and 3b., respectively.

Microstructure analysis by SEM reveals that the samples contain closed pores with high sphericity. The Hastelloy X fibres are distributed in the glass matrix between the pores. The interface between fibres and glass matrix is sharp, indicating that the wetting of Hastelloy X fibres by borosilicate glass during microwave heat-treatment has been good, with no cracking observed at the interfaces.

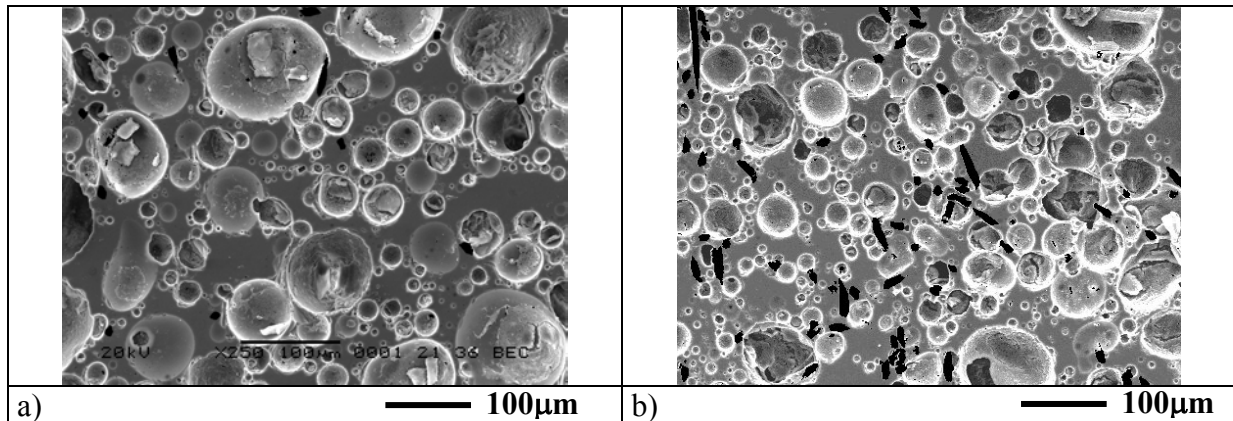


Fig. 3. Enhanced SEM images of foamed samples using SiC auxiliary absorber: a) fibre volume fraction = 2 %, b) fibre volume fraction = 10 %.

Little agglomeration of the stainless steel fibres was detected. Moreover, the fibers seem to be located preferentially in the proximity of pores, indicating that the fibres may be pinning the expanding pores. Moreover, it has been observed that stainless steel fibres appear to have prevented growth of pores in the 10vol% fibre sample. This indicates that increasing the volume fraction of fibers limits pore growth and leads to a more even distribution of smaller pores in the glass foam composite. Moreover, the higher volume fraction of fibres led to less distortion of samples during microwave heating. The samples with 10vol % fiber retained their cylindrical shape, whereas samples with 0 and 2vol % fibres severely deformed during heating.

Direct microwave heating

The heating of the samples placed on the refractory block in the single mode microwave applicator, without using SiC auxiliary absorbers, was sensitive to the sample position and orientation in the waveguide. Most of these samples did not experience significant heating even after 3 to 4 minutes in the maximum electric field. However, samples containing 2vol% Hastelloy X fibres, positioned vertically in the electric field, did heat however only in a small ribbon-like area at the centre of the sample. The temperature recorded by the optical pyrometer reached 825°C in approximately 3 minutes. A macrograph of this sample is shown in fig. 4a, where foaming is clearly visible in the centre of the sample whilst the edges remained powdery and unsintered. The same samples did not heat efficiently when positioned horizontally on the refractory block. In this case the temperature remained below the detection threshold of the pyrometer (600°C). Samples containing 10% fibres did not heat efficiently in any orientation or position when placed on the refractory block.

Samples containing 2vol % Hastelloy X fibres were processed under alumina powder with the cylinder axis in the vertical direction in the centre of the waveguide (high electric field). These samples failed to sinter or to show significant temperature rises even after 5 minutes of exposure to the field.

The same samples, when rotated so that they were in horizontal position with their axis perpendicular to the waveguide, heated very rapidly whilst under alumina powder, reaching temperature in excess of 800°C in less than 40 s. A macrograph of such a sample is shown in fig. 4b. Some alumina powder can be seen, adhered to the surface of these samples, due to the high temperatures achieved.

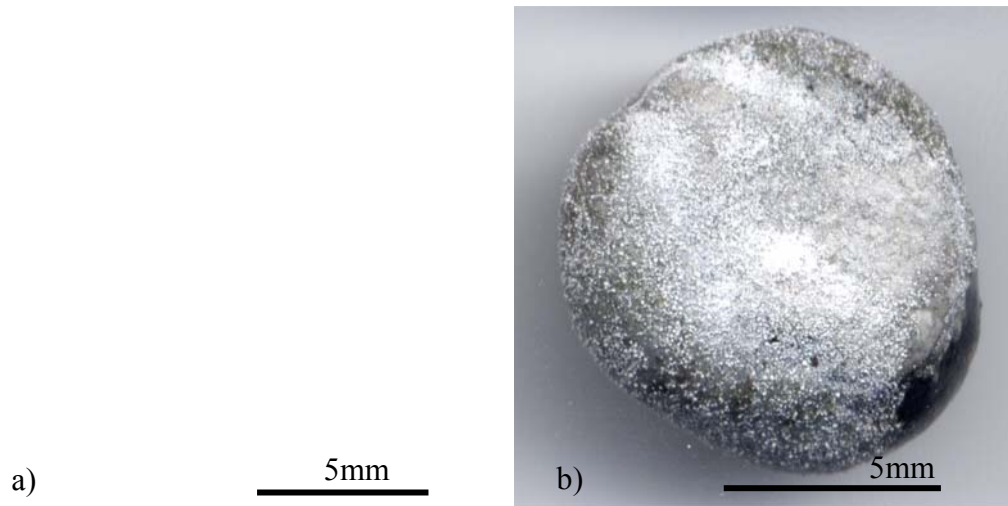


Fig. 4. Optical macrograph showing: a) the uneven heating of a 2vol% Hastelloy fibre containing sample processed on a refractory block, in the centre of the applicator, with the cylindrical axis horizontal and perpendicular to the length of the wave guide as shown; b) a 2vol % Hastelloy X fibre containing sample heated successfully by microwave radiation under alumina powder in the area of high electric field

Samples containing 10vol% fibres under alumina powder in the area of high electric field heated to temperature higher than 800°C in less than 5 minutes. On a macroscopic scale the sintering was uniform across the samples, which exhibited limited shape distortion (bloating). The samples foamed during processing, in agreement with results using a SiC susceptor presented above. The 2vol% fibre containing samples proved much easier to heat rapidly under alumina powder at the side of the applicator, in the region of high magnetic field, or mid way between the center and the side of the applicator, where the electric and magnetic fields are both fairly high.

Samples sintered in the magnetic field showed a very inhomogeneous distribution of metallic phase after processing. Most of the Hastelloy X fibres underwent melting and coalescence to form a few large areas of solidified metal in the final sample. One such areas is shown in fig. 5a for a 2vol% sample. Increasing the volume fraction of the fibres to 10% but keeping the sample in the high magnetic field resulted in a different microstructure, shown in fig. 5b. These samples contain some non spherical pores. Evidence of melting and coalescence of the Hastelloy X fibres is not apparent, even in areas where fibres were in close proximity to each other.

Sintering the 10vol% samples in the electric field region resulted in better sintering behaviour. Spherical pores can be observed in fig. 5c and no reaction between the metallic fibres and glass matrix was apparent. There was no evidence of interaction between fibres or melting of fibres.

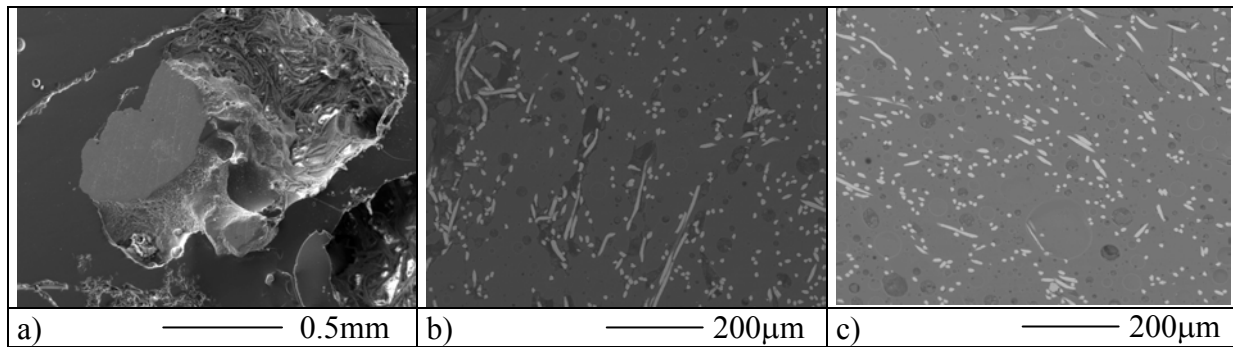


Fig. 5. SEM micrographs of: a) metallic lump (light grey) near fibre agglomerate in a 2vol.% fibre sample heated in the magnetic field region; b) 10 vol.% fibre sample heated in maximum of H-field area; c) 10 vol.% fibre sample heated in maximum of E-field area

5. DISCUSSION

The formation of porosity in the present composites may be explained following similar arguments as those presented in our previous investigations on porous Mo particles reinforced borosilicate glass matrix composites [14].

Foaming is ascribed to gas evolution from the molten glass matrix, which, above the glass transition temperature (T_g), undergoes thermal runaway, increasingly absorbing microwaves, becoming thus more "microwave active" as its temperature increases. This phenomenon occurs locally, since it depends on the local electric field strength and on the dielectric properties of the material, which, being multi-phased, vary locally too. Thus, when the SiC element is used as auxiliary absorber, in the 0 vol% sample, the portion in contact with the SiC is heated first, and as it reaches the T_g , it undergoes thermal runaway, swelling and foaming, while the cooler surface layers, exposed to air, remain almost unaltered. In addition, due to the low thermal conductivity of the samples, bubbles tend to form only in a relatively small region, which should absorb most of the microwaves energy. Thus, large pores are formed, and the sample shape is lost due to the low viscosity of the melt. The 2 vol% samples exhibit a similar behavior, due to the small amount of reinforcement. Increasing the fibre content, up to the 10 vol%, the system drastically changes its behavior: electric field is concentrated in proximity of the fibers' tips, the overall composite loss factor becomes higher and thermal conductivity increases. The combination of these factors should lead samples to absorb more homogeneously the microwaves, and to better conduct the generated heat. Moreover, the fibres' tips may act as "nucleating agents" for pores, since the higher local electric field strength associated with their shape factor should lead to higher power dissipation in the surrounding matrix. With increasing vol. fraction of fibres, these should act as a barrier to pore growth, since they form a kind of interpenetrating network, leaving limited free space in the matrix for the pores to expand and coalesce.

In direct microwave heating conditions, i.e. without a SiC element, the uneven heating of samples placed on top of the refractory brick in the magnetic field sector can be associated to an excessively localized heating of the conducting phase, in presence of a low thermal conductivity matrix. This prevents the material adjacent to hot fibers from homogeneously reaching a temperature at which it is able to couple efficiently with the microwave radiation so that a very large temperature gradient is created across the sample. On the other hand, if the samples contain a higher fraction of metallic fibres (10vol%), and therefore a higher effective thermal conductivity, the heating may not be as efficient due to surface heat losses. Thus, only the 2 vol% samples could be heated without further insulation of the system.

Placing the samples under alumina powder reduced surface heat losses from the samples and this resulted in more homogeneous heating of the 2vol% samples when heated with their axis in horizontal position in the electric field area. The 2vol% samples could not be efficiently

heated in other orientations in the region of high electric field due to the relatively low volume fraction of metal fibres being inefficient at coupling with the microwaves.

Increasing the volume fraction of fibres to 10vol% had the effect of obtaining more coupling sites with the microwaves at lower temperatures. Thus when the 10vol% containing sample was insulated from the air by alumina powder, it could be more easily heated in any orientation.

When the 2vol% samples were heated in the high magnetic field very high temperatures were achieved. The glass quickly became fluid and the Hastelloy X fibres were able to sink in the glass and coalesce in a few molten agglomerates (figure 5a). The fluidity also caused the pores in the centre of the samples to collapse. Moreover, some of the fibres evidenced localized melting, which may be related to local arcing induced by the high electromagnetic field. The 10vol% fibre containing samples were also successfully sintered in the magnetic field. The increased conductivity of the samples caused more uniform heating and fewer local hot spots. This resulted in lower overall temperatures, lower fluidity of the glass, no melting of the metallic fibres and the retention of a few pores which did not collapse in the samples (figure 5b).

6. CONCLUSIONS

The application of microwave radiation as the heating source for the processing of glass matrix composite foams containing Hastelloy X fibres was demonstrated using two different heating conditions and experimental set-ups. A fibre volume fraction of 10% led to an improved distribution of smaller pores in the material. Porosity levels of >50% were achieved in all composites. Samples with 10vol% fibres fabricated using the auxiliary SiC microwave absorber element were the best produced; they exhibited uniform pore size distribution and retained their macroscopic shape. Pore formation is attributed to gas evolution from the molten matrix, which probably is subjected to microwave thermal runaway, up to an extent depending on the fibre volume fraction. It is also suggested that fibres act as nucleating agents for pore formation. The auxiliary absorber contributes to the reduction of thermal gradients and to the raise of the temperature of the samples up to a level at which they start effectively coupling to microwaves. However, it has been proved here for the first time that a proper amount of metal fibres addition is sufficient to raise the temperature of the glass to a point at which it is able to couple effectively with the microwave radiation without the requirement of an additional susceptor. In this case, sintering occurred in less than 3 minutes in both areas of high electric and of high magnetic microwave fields.

The combination of high porosity and metal fibre toughening should lead to composites of high thermal shock resistance suitable for thermal protection systems. The quantitative characterization of mechanical properties and thermal shock behaviour of the prepared foams is the focus of current research.

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